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In Line Monitoring of VAc-BuA Emulsion Polymerization Reaction in a Continuous Pulsed Sieve Plate Reactor using NIR Spectroscopy

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Summary: This work deals with the in line and in situ monitoring of the changes in residual monomer concentrations and polymer particle size in the process of emulsion copolymerization of vinyl acetate (VAc) and butyl acrylate (BuA) over the sections of a novel tubular reactor (pulsed sieve plate continuous reactor, PSPC) using NIR spectroscopy. Off-line measurements (gas chromatographic, gravimetric and dynamic light scattering) were used as reference for the development of the multivariate PLS calibration model. All NIR spectra were on-line collected with an IFS 28/N Bruker spectrometer using a probe (transflectance mode) immersed into the reaction medium. The calibration model and validation data were analyzed using the OPUS/QUANT software. The results indicated that there exists a good agreement between values from the NIR calibration models and the off-line reference measured experimental data. Moreover, the on-line NIR can detect efficiently the occurrence of disturbances during the polymerization reaction, a useful tool for the improving the process safety.

Keywords: emulsion polymerization; NIR spectroscopy; pulsed sieve plate continuous reactor

Introduction

Emulsion polymerization processes are widely used for the industrial production of different commercial products, such as paints, adhesives and varnishes that are typical applications of filming-forming latexes and can be carried out with a great variety of monomers in different types of reactors (batch, semicontinuous and continuous). This polymerization process occurs in a heterogeneous medium composed by water as continuous phase, emulsifiers, monomers, water-soluble initiator and additives. Due to the multiphase character and compartmented nature, high molecular weights and high polymerization rates can be achieved thus favoring higher productivity and lower residual monomer contents in the final latex composed of submicrometric polymer particles. The monitoring and supervision of the monomer concentration and the growth of particle size along emulsion polymerization reaction, besides to estimate of the overall conversion, the copolymer composition and number of particles calculated from the variables above, guarantee the high quality of the final product whenever exist tools to provide continuous fast and accurate answers, thereby improving, for example, reaction time and process safety. Vibration spectroscopy methods, such as near infrared (NIR) and Raman spectroscopies are some of the few analytical techniques that enable the observation of the evolution of reaction chemistry, having a high sampling flexibility as well

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as reducing exposure time of laboratory personnel to chemical hazardous.

Currently, the use of sensors that allow the in line monitoring has been studied and applied in order to monitor and control the in line process, ensuring quality product in industrial reactors, thereby minimizing the traditional laboratory techniques, which demanded time for obtaining information and delay the process in making decisions.[1]

The combination of NIR spectroscopy with immersion probes and optical fibers offers a non destructive and non invasive possibility of remote monitoring either in reactors or in process streams, transforming it in a versatile technique, with an easy manipulation and fast acquisition of physical and chemical information. However, the information acquired in line (*hard sensors*) is not a direct measurement on the variable in analysis, requiring, therefore, mathematical and statistical procedures on the physical and chemical phenomena of the process (*soft sensors*). The combination method-tool is essential for application in the monitoring of emulsion polymerization reactions.

In literature, many papers reported about successful investigation dealing the possibility of in line monitoring of emulsion polymerization processes using NIR spectroscopy (NIRS). Wu et al.[2] used the SW-NIR spectroscopy of (short-wavelength near infrared) in the range of 700 to 1100 nm for the in line monitoring of emulsion polymerization of styrene (S). Vieira et al.[3] found that it is possible to detect the presence of droplets of monomers in a polymer latex from the NIR spectra collected during an emulsion polymerization of methyl methacrylate (MMA) and butyl acrylate (BuA) enabling a considerable improvement in the control of emulsion polymerization processes and the final quality product, since the presence of drops of monomer can cause degradation in the control of reactions, and increase the risk of sudden increases in temperature located.

Later, Vieira et al.[4] used the technique of NIR spectroscopy for monitoring simultaneously the monomer and polymer concentrations in line and in situ of a seeded semibatch emulsion copolymerization) of methyl methacrylate and butyl acrylate. Reis et al.[5] verified the correlation between NIR spectra, collected by a transflectance immersion probe, and average particle diameters of styrene and butyl acrylate emulsion copolymerizations. And Reis et al.[6] described the in-situ and in line estimation of monomer concentrations and average particle sizes by NIR spectroscopy using a transflectance immersion probe during semicontinuous styrene and butyl acrylate emulsion copolymerizations. In this work the independence of the average particle size spectral information from monomer and polymer concentrations was verified. All works described above were conducted in batch and semicontinuous reactions, researches related to spectroscopic monitoring of continuous polymerization reactions conducted in tubular reactors or in CSTRs are invalid or not widely used in the literature open. In the industry, continuous reactors present the advantages of lower volumes and better control of polymer quality due the reduction of batch-to-batch variations. However, in relation to CSTRs these may exhibit self-sustained periodical oscillations in monomer conversion and particle sizes. These oscillations can be minimized or avoided in tubular reactors with pulsed flow, due to a lower level of axial dispersion; moreover, tubular reactors present further advantages such as higher operational flexibility, less off-spec product due to shorter transients during startup, shutdown and grade transitions, and better temperature control due to the higher heat transfer area-to-volume ratio.[7] More specifically in reference to pulsed continuous reactors these actually can be of three types: pulsed column (PC),[8,9] pulsed *filled* column (PFC) [10] and pulsed sieve plate column (PSPC).[11,12] In both cases, pulsations produce sufficient turbulence to avoid depositions, clogging and fouling by the polymeric particles. Recent publications [7,11,13,14,15] studied vinyl acetate and butyl acrylate emulsion

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homo- and copolymerizations in a PSPC and showed that the presence of sieve plates combined with pulses allowed to minimize radial temperature and concentration gradients, as well as, coagulation formation. In addition, the amplitude and frequency of the pulses may also be used to vary the axial dispersion along the column, which in turn may affect polymer properties.[8–10,16–18]

This work deals in line monitoring of changes of monomers concentrations and the average size of particles of the emulsion copolymerization of vinyl acetate and butyl acrylate (VAc-BuA) over the sections of a PSPC reactor using NIR spectroscopy. Copolymerization reactions carried out in a stirred tank reactor (STR) were used for the development of NIR calibration models, and reactions carried out in the PSPC are used to validate the proposed models. Experimental techniques such as gravimetry and gas chromatography (GC) were used to determine off-line concentration of residual monomers and the correlation spectroscopy of the photons was used in determining the size of the particles. All spectra were collected (for both calibration and validation) through a NIR probe for immersion in the way of transflectance.

Experimental Part

The following reactants were used in the emulsion copolymerizations: industrial grade vinyl acetate, butyl acrylate that were provided by BASF Brazil, acrylic acid as functional monomer and sodium lauryl sulfate (SLS) emulsifier were obtained from Neon Ltda., water soluble initiator: sodium persulfate ($Na_2S_2O_8$) was from Labsynth Ltda., buffer: sodium carbonate (Na_2CO_3) was obtained from Maia Ind. e Comercio, polyvinyl alcohol (PVA) as colloidal protector supplied by Vetec Química Fina Ltda., distilled and deionized water and hydroquinone to shortstop reaction of the collected samples.

The global conversion estimated was evaluated by gravimetric methodology and copolymer composition was calculated from residual monomer concentrations measured by GC employing a headspace gas chromatograph (Shimadzu HS-GC-17 A). Photon correlation spectroscopy (Coulter N4 Plus), with a photon incidence angle of 90°, was used as reference technique for the off-line measurement of the average particle diameters.

The Table 1 describes the general recipe used throughout the all emulsion polymerization reactions (STR and PSPC reactor) and the Table 2 includes the operational and characteristics parameters of the reactions. All reactions were developed with a final polymer content of 20%.A detailed description of the strategies monomer feeds and the comparison of these two reactors (STR and PSPC) used in the development of this work have been published in a previous work of the research group.[15]

Under the conditions indicated in Table 2 for the PSPC, the values of the axial dispersion coefficient and net fluid velocity are $D_{ea} = 2.2\,\text{cm}^2/\text{s}$ and $v_Z = 0.27\,\text{cm/s}$, respectively. The net fluid velocity was calculated by the flow rate divided by the cross section area, and the axial dispersion coefficient was evaluated from an empirical correlation previously developed for the same equipment.[18]

All NIR spectra were on line collected with an IFS 28/N Bruker spectrometer, equipped with a quartz bean splitter, using a probe (Hellma 661.622 NIR, with a transflection system with overall light path equal to 1 mm) immersed into the reaction medium. The spectra measurement collect in the STR were used as reference for the

Table 1.
Recipes VAc – BuA emulsion copolymerizations.

Reagents	% wt fraction
Water	0.792
Emulsifier (SLS)	0.012
Initiator ($Na_2S_2O_8$)	0.006
Agent buffer (Na_2CO_3)	0.001
VAc*	0.161
BuA*	0.028

*The initial ratio between the monomers was VAc = 85%, BuA = 15%.

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Table 2.
Operational characteristics of the reactors.

Description	Batch Reaction in STR	Intermittent Batch Reaction in STR	Semicontinuous Reaction in STR	Continuous Reaction in PSPC
Peclet number	–	–	–	61
Amplitude of pulses	–	–	–	18 mm
Frequence of pulses	–	–	–	2.1 Hz
Jacket temperature [a]	55 °C ± 1°C	55 °C ± 1°C	55 °C ± 1°C	55 °C ± 1°C
Residence time	–	–	–	30 minutes
Total reaction time	150 minutes	150 minutes	150 minutes	150 minutes
Internal Volume	3 liters	3 liters	3 liters	6 liters

[a] The jacket temperature was controlled (PI controller) by the mixture of hot and cold water streams.

development of the multivariate NIR calibration model developed at the OPUS software using the program QUANT2.

Figure 1 presents schematic representation the tubular reactor NIRS system used in this work.

Results

Three models were developed NIR calibration in order to monitor the evolution of residual VAc and BuA concentrations and particle size in the PSPC sections. Due to the low amount of BuA in the reaction medium (ratio of initial monomers VAc-BuA equal to 85–15, see Table 1) some problems may occur in the samples elaborates with traditional techniques that could provide some small fluctuations in the data due to difficulty in withdrawing samples of latex mainly in intermediate sections.

NIR Model for Residual VAc and BuA Concentrations

Ten reactions carried out in a STR using different strategies of feeding of monomers in order to elaborate NIR calibration model (two reactions in batch, two reactions in intermittent batch reactions and six in semicontinuous reactions).

The temperature in all reactions was maintained at approximately 55 °C and the agitation speed kept at 200 rpm. For obtaining reference data methods of gravimetry and gas chromatography (GC) were used to determine the concentrations of residual monomers.

The spectral region chosen for residual VAc was the first region overtone (6212–6187 cm^{-1}) wherein is identified a band which is attributed to the consumption of monomer. The calibration model used to second derivative with 25 points smoothing as spectral pre-processing and the cross-validation as internal validation. Three principal components were used with a high correlation coefficient ($R^2 = 0.9858$).

The spectral region chosen for residual BuA was in the first region overtone (6173–6159 cm^{-1}) which is also attributed the decrease of the residual monomer concentration. The BuA calibration model also used the second derivative with 25 points smoothing as spectral pre-processing, and cross-validation as internal validation. Four calibration model were used with a $R^2 = 0.9383$. The low correlation about the model of residual VAc can be attributed to the experimental sensitivity that exists for the low concentration of monomer and high speed of reaction displayed.

The Figure 2 show the results of the validation of residual VAc BuA models in the sections 2 (upper graphs) and 4 (lower graphs). According this Figure VAc and BuA models follow successfully the monomer concentrations along the reaction. Also can be deployed the ability to detecting latex in the points of sampling before the first time of residence (first 30 minutes of reaction) which is difficult to be identified by traditional techniques of sampling. The detection is identified as a rapid oscillation in the first points that representing the concentrations, once reached the first

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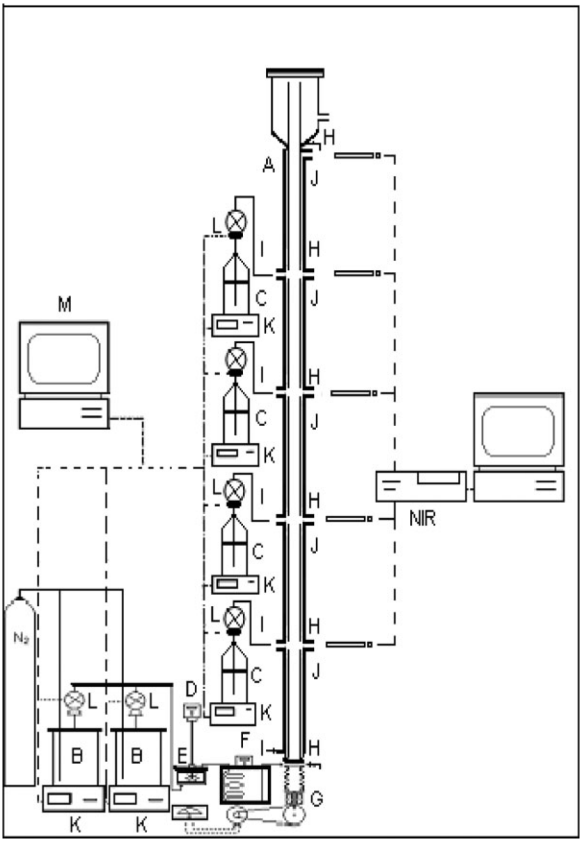

Figure 1.
Schematic representation PSPC reactor and NIRS system: A-Reactor, B,C-feed tanks, D-agitator, E-pré-mixing tank, F-heater, G-pulsator, H-sampling points, I- jacket entrances, J- jacket outlet, K-balances, L-metering pumps, M-computer.

residence time; models consistently monitored concentrations.

NIR Model for Average Particles Size

The sensitivity of NIR in the monitoring of particles of VAc-BuA along emulsion polymerization process in the transflectance mode was evaluated. The spectral range used for determining the size of the particles was 9485–12989 cm^{-1}, in this region the baseline of the spectra have significant deviations attributed to the light scattering and is much more intense compared to other spectral bands of the NIR wherein the absorbance is predominant.

Ten reactions were carried out with different strategies of monomers and initiator feeding in order to obtain different sizes of final polymer particles that varied in the range of approximately 50 nm to 150 nm.The first derivative with 17 points smoothing as spectral pre-processing and cross-validation as internal validation, besides, seven principal components with a correlation coefficient $R^2 = 0.9604$ were enough to elaborate a NIR calibration model for evolution of the particle size .The external validation of the NIR model for the average particle sizes is shown in Figure 3 where it is observed the monitoring of the particle growth successfully along the last sections (sections 4 and 5). The model was validated with experimental data acquired by the photon correlation spectroscopy (dynamic light scattering, DLS) after first residence time.

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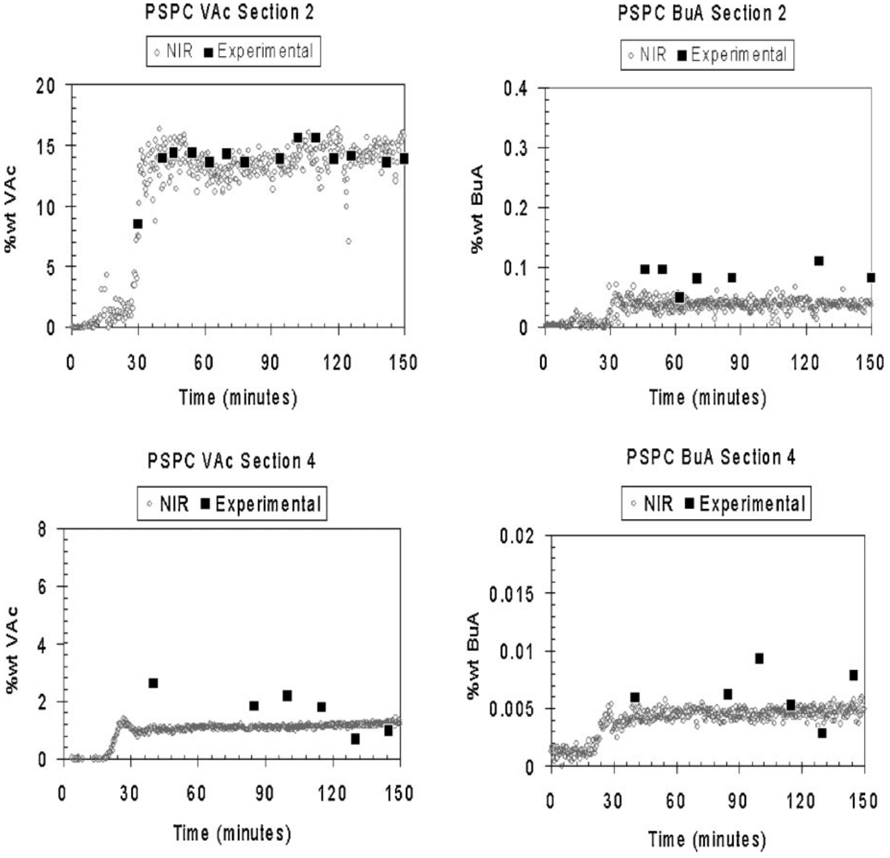

Figure 2.
Validation of NIR models the evolution of the residual VAc and BuA concentration along section 2 (upper graphs) and section 4 (graphic below) of the PSPC, circles: NIR data, dark squares: experimental data through GC.

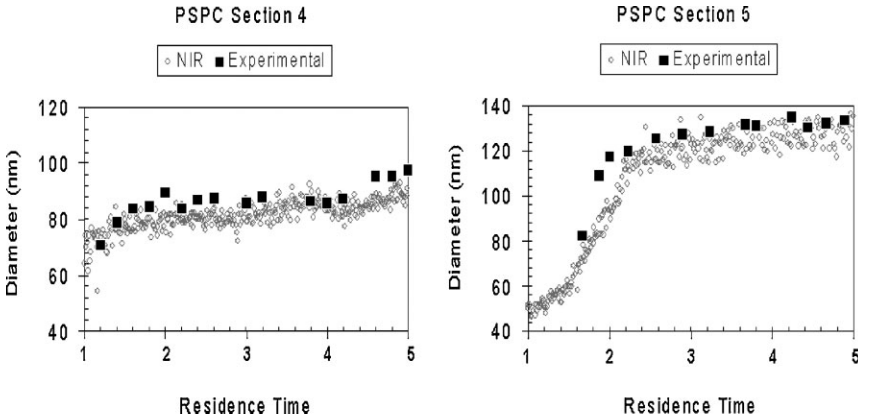

Figure 3.
In-line monitoring of average polymer particles size in section 4 (right) and section 5 (left) in the PSPC, circles: NIR data, dark squares: experimental data through DLS.

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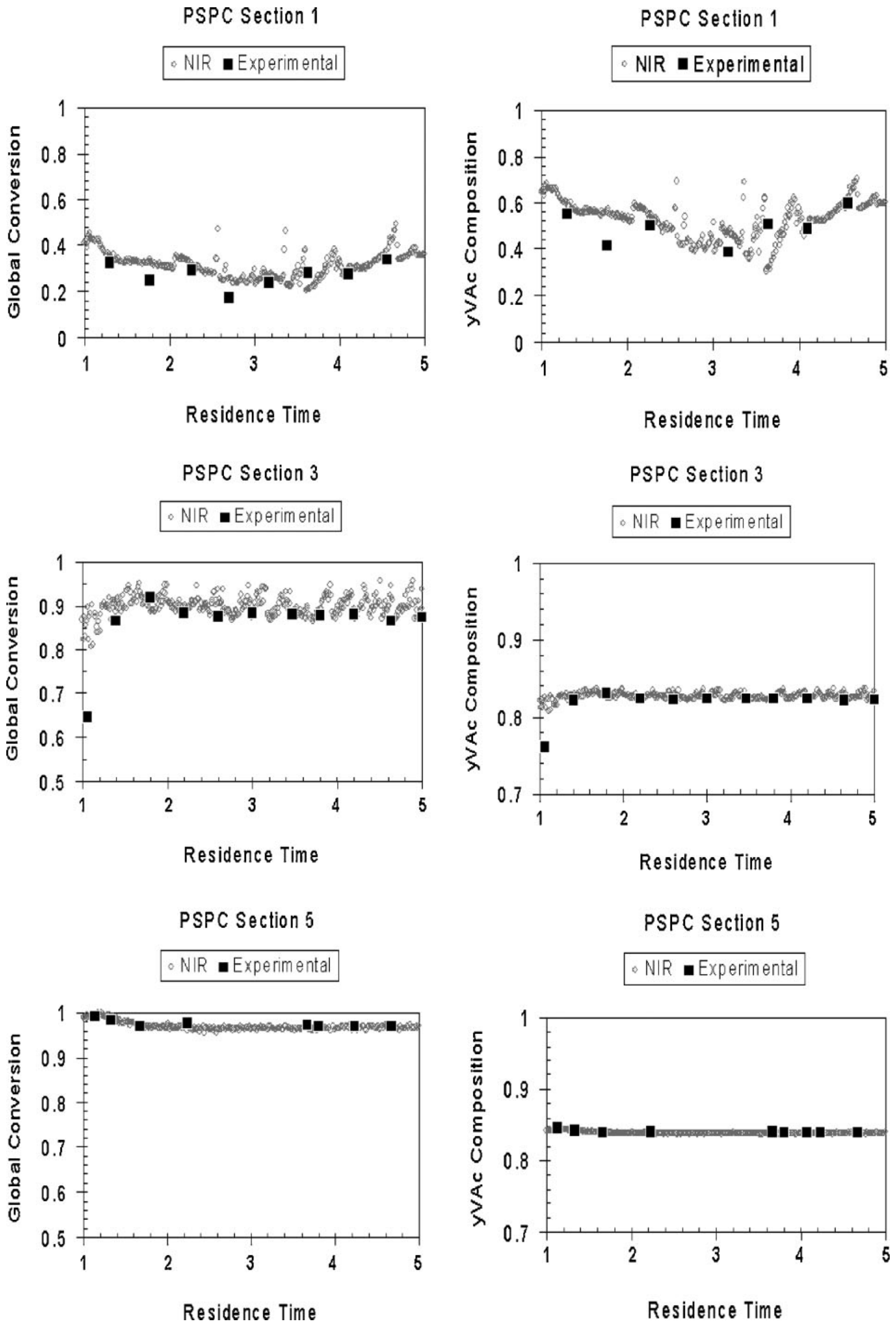

Figure 4.
Validation of the global conversion and VAc composition along the section 1, 3 and 5 during polymerization reaction (1 to 5 residence time).

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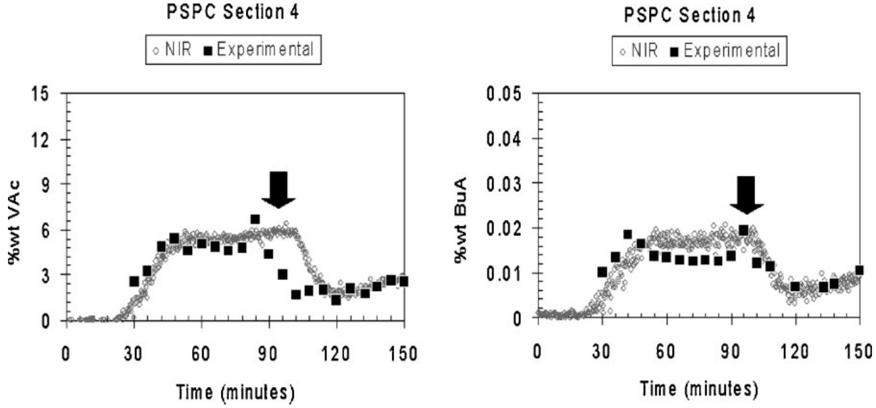

Figure 5.

In line detention of operational disturbance during the reaction. circles: NIR data, dark squares: experimental data, arrow: start disturbance operational.

Estimate of the Global Conversion and Copolymer Composition

From the NIR models of residual VAc and BuA concentrations can be estimated the global conversion and copolymer composition of the sections of PSCP. The Figure 4 shows the experimental estimates and NIR prediction of the global conversions (Figures on the right side) in the first (upper graphs), third (intermediate graphs) and fifth (lower graphs) sections and the copolymer composition VAc (Figures on the left side) in PSPC. The results show good agreement between the experimental data and predicted estimates confirming the possibility of in-line monitoring and in situ.

In Line Identification of Operational Disturbance

In the Figure 5 was observed the detention capacity front the disturbance operational such as zero flow rate and shortstop monomer feeding in the reaction. These results can possible to act immediately on the system in real time, thus guaranteeing, the security of the process and the laborers.

Conclusions

This work showed the feasibility of inline monitoring and in situ of reactions in emulsion copolymerization of VAC-Bua using NIR spectroscopy in each of the sections of the PSPC. Were used the second derivative with 25 points of smoothing and first derivative with 17 points of smoothing as spectral pre-treatments for monomer concentrations and size average particles, respectively, obtained high correlation coefficients. The validations of the NIR model with data obtained in the PSPC observed an acceptable agreement between experimental data and predicted. Additionally, the values predicted by the NIR models also served to estimate the evolution of global conversion and copolymer composition into the reactor sections, the results observed between the estimated experimental and NIR were satisfactory. Finally, the NIR spectroscopy was tested against its ability to operational disturbances, the results indicated that NIR successfully detect this type of disturbance (such as zero flow rate and shortstop monomer feeding the reactants in a reaction) allowing the possibility of action on the system. Further work of the research group will be made in order to achieve a simultaneous monitoring along the sections of the tubular reactor.

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